Solar Light Driven Photocatalytic Activity of TiO$_2$ Coupled Bi$_2$O$_4$ Nanocomposites

T. Vimala$^{1,2}$, A. Sivarajan$^1$*, T. Rajachandrasekar$^3$ and K. Veeravelan$^3$

$^1$Department of Chemistry, Govt. Arts College, Tiruchirappalli 620 022, (Affiliated to Bharathidasan University), Thiruchirappalli- 24), Tamilnadu, India  
$^2$Department of Chemistry, S.T.E.T. Women’s College (Autonomous) (Affiliated to Bharathidasan University, Thiruchirappalli- 24), Mannargudi 614 016, Tamilnadu, India  
$^3$Photocatalysis Laboratory, Department of Chemistry, M.R. Govt. Arts College, Mannargudi 614 001(Affiliated to Bharathidasan University, Thiruchirappalli- 24), Tamilnadu, India

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ABSTRACT

TiO$_2$/Bi$_2$O$_4$ nano composite photocatalyst was synthesized by sol-gel method. The chemical composition morphology and micro structural features of the materials were characterized by Fourier transform infrared (FT-IR) spectroscopy, X-ray diffraction (XRD) analysis, scanning electron microscopy (SEM) with energy dispersive X-ray (EDX) analysis and UV-vis-diffuse reflectance spectroscopy (UV-vis-DRS). The synthesized nano composite were used as photocatalyst materials for the degradation of Eosin Yellow (EY) dye under solar light irradiation. The effect of pH and reusability were studied. The mechanism of photocatalytic degradation also discussed.

Key words: Eosin Yellow, Nanocomposite, Photocatalytic degradation, TiO$_2$/Bi$_2$O$_4$

Introduction

Dyes, in particular azo dyes, are the major by-product of the textile industry dyes have been used to color textiles in order to provide a variety of fabrics to choose from, but at the cost of polluting the environment. It has been estimated by the World Health Organization (WHO) that 17-20% of industrial water pollution is caused by the dyeing treatment of textiles, while about 80% of the dyeing process is done using azo dyes. Azo dyes are known to have acute carcinogenic effects to human and a negative impact on the environment. Hence it is becoming a global urgency to mitigate this issue (Hasan et al., 2021). The semiconductor-assisted photocatalysis process has proven to be effective for the decomposition of organic pollutants. Such as acids, dyes and aromatic and phenolic compounds, etc., (Gowthami et al., 2018) which are present in wastewater, due to its strong redox potential, environment friendliness, (Gowthami et al., 2020) moderate operation temperature, easy operation and useful final products (Muthuvel et al., 2014). Nano structured semiconductors show great potential for environmental remediation because of photocatalytic oxidation, (Hu et al., 2017) which is activated under the solar light or UV light (Liu et al., 2015). This has prompted the scientific community to effectively develop elimination technologies, which are known as advanced oxidation processes (AOPs) (Feizpoor, et al., 2018). These processes are based on the production of hydroxyl radicals which are strong oxidizing agents for mineralizing organic pollutants. Among the various AOPs attention has been paid to
semi-conductor photocatalysts (e.g. TiO₂) (M’Bra, et al., 2019). By far the most researched photocatalytic material is anatase TiO₂ because of its long-term thermodynamic stability. Strong oxidizing power, low cost and relative non toxicity (Tan, et al., 2013). However, the rapid recombination of electrons and holes is one of the main reasons for the low photocatalytic efficiency of TiO₂. (Alizadeh, et al., 2019) Moreover its wide band gap of 3.2 eV (Cheng, et al., 2018). Recently, a new visible-light-driven photocatalytic of Bi₂O₄ was synthesized and used to photodegrade organic contaminants (Hameed, et al., 2015). It is a simple oxide with a narrow band gap (~2.0 eV) and a mixed valence of Bi³⁺ and Bi⁵⁺, exhibiting better photocatalytic activity than other visible light catalysts such as CdS and Bi₂O₃ (Xia, et al., 2017). Therefore, in this study, we have design the Bi₂O₄ modified TiO₂ heterojunction photocatalyst by the sol-gel method. The photocatalytic activity of the TiO₂/Bi₂O₄ nano composite under solar-light irradiation was explored by using EYosin Yellow (EY) dye. In addition, a possible mechanism for degradation was also proposed.

Experimental

Materials

The commercial Eosin Yellow (EY) dye (C.I. No. 45380), Titanium isopropoxide, isopropanol (AVRA Chemicals), sodium bismuthate (Hi-Media) were used as received. The experimental solution was prepared using distilled water.

Methods

Fabrication of the TiO₂/Bi₂O₄ Catalyst

Sodium bismuthate (NaBiO₃.2H₂O) was dispersed in deionized water (60 ml) and stirred at room temperature for 10 min to form a suspension. The resulting suspension was loaded into a Teflon-linked stainless steel autoclave with a capacity of 100 ml and maintained at 160°C for 12 h. After cooling, the resultant product was washed three times with described water and ethanol and then dried overnight in an oven at 60°C. 19 wt% of Bi₂O₄ was mixed with an appropriate amount of titanium isopropoxide (12.5 ml) and isopropanol (80 ml) solution. The mixed suspension is stirred for 6 h. The precipitate was filtered, washed with deionized water several times, and dried in a hot air oven at 80°C for 6 h. A TiO₂-Bi₂O₄-coupled system is taken in a silica crucible and calcined at 450°C for 12 h in a muffle furnace at the rate of temperature increase of 20°C/min. After 12 h, the furnace is allowed to cool down to room temperature. The TiO₂/Bi₂O₄ catalyst is collected and used for further analysis. This catalyst has 19 wt% Bi₂O₄ and catalyst. Similarly, 13, 16, and 21 wt% of Bi₂O₄-coupled TiO₂ are prepared using an appropriate amount of Bi₂O₄. The bare TiO₂ catalyst is prepared using this procedure without Bi₂O₄. Photocatalytic Degradation Experiments and Characterization Techniques are reported earlier (Gowthami, et al., 2020)

Results and Discussion

FT-IR and XRD analysis

The FT-IR spectra of the prepared TiO₂, Bi₂O₄ and TiO₂/Bi₂O₄ nanocatalyst are shown in Figure 1. The OH stretching vibrations are observed in the range of 3421-3417 cm⁻¹ for all the samples. In Figure 1a, the absorption bands at 600-400 cm⁻¹ are attributed to the Ti--O group, respectively (Feizpoor, et al., 2018). In Figure 1b the band located at 414 cm⁻¹ is corresponded to the Bi–O vibration (Khazaee, et al., 2019). Figure 1c show that both Ti-O and Bi–O stretching vibration are observed in the range of 600-400 cm⁻¹. The obtained results provide evidence that Bi₂O₄ is loaded effectively on TiO₂. The crystal structure of TiO₂, Bi₂O₄ and TiO₂/Bi₂O₄ catalysts was studied by powder XRD analysis as shown in Figure 2. The characteristic peaks of TiO₂ at 20 values of 25.3, 37.7, 47.9 and 54.9° match with (101), (004), (200) and (105) planes of TiO₂ (JCPDS No. 21-1272).
VIMALA ET AL

Figure 2b reveals that the rod-like Bi$_2$O$_4$ is ascribed to the monoclinic phase of TiO$_2$/Bi$_2$O$_4$ sample which shows the presence of Ti, Bi and O by the appearance of Ti, Bi and O peaks without any other characteristic peaks. Hence, the EDX results are perfect evidences to propose that the prepared sample does not contain any other elements and is indeed free from other impurities.

UV-Vis-DRS

To understand the light absorption capacity of the as-prepared photocatalysts, the UV-Vis diffuse reflectance spectra of TiO$_2$, Bi$_2$O$_4$ and TiO$_2$/Bi$_2$O$_4$ are detected (Figure 5A). As we can see that the absorption edge of TiO$_2$ locates at the UV range, the absorption threshold wavelength of Bi$_2$O$_4$ is about 620 nm and strong absorption is observed in the visible light region. Compared to TiO$_2$, TiO$_2$/Bi$_2$O$_4$ heterostructures have obvious red shift phenomenon, confirming the successful incorporation of Bi$_2$O$_4$ into TiO$_2$. In general, the wider is the visible light response range and higher visible light absorption intensity, the better is the visible light photocatalytic activity of photocatalyst. From the K.M. plot, the band gap energy was estimated at 3.23, 1.97, and 3.19 eV for TiO$_2$, Bi$_2$O$_4$, and TiO$_2$/Bi$_2$O$_4$, respectively (Fig. 5B).

Primary analysis

The photocatalytic activities of EY with TiO$_2$/Bi$_2$O$_4$ catalysts using solar light under different conditions are shown in Figure 6. The dye is resistant to direct photolysis by solar light (curve a). There is a small decrease in concentration of dye observed when it is
treated with TiO2/dark for 90 min (curve b). When the dye was put on irradiation with TiO2 under solar light, 54% percentage of degradation was observed at 90 min (curve c). A small decrease in dye concentration (27%) occurred when it was treated with dye/TiO2/Bi2O4/dark (curve f) for 90 min. The degradation of dye on irradiation with TiO2/Bi2O4 catalyst of different wt% of Bi2O4 is shown in curves d, e, g, and h, and catalyst with 19 wt% TiO2/Bi2O4 shows a higher degradation (curve g, 91%). Hence, 19 wt% of Bi2O4 is taken as optimum concentration of Bi2O4 on TiO2 for further studies.

**Effect of pH**

The effect of pH value of solution on the degradation and decolorization of EY was studied in the range of 3-9 and the results were shown in Figure 7. The percentage of degradation (76 to 95%) and decolorization (80 to 98%) was found to increase with an increase of pH from 3 to 6 at 90 min. As it was expected, the complete degradation and decolorization was achieved in the investigated pH range at the optimum pH of 6. Further increase in pH above 6 causes the percentage of degradation and decolorization to decrease. Above pH 6 this value the TiO2/Bi2O4 surface is negatively charged. It is expected that at pH 6, there is a strong interaction between negatively charged catalyst and dye cation consequently (Muthuvel et al., 2020). The optimum pH is 6.

**Reusability**

Estimating the stability and reusability of photocatalytic is indispensable for the practical application of TiO2/Bi2O4. The dye concentration of EY was kept constant at 1×10^{-4} M and was exposed to solar light irradiation 120 min for each cycle. The catalyst dosage of photocatalyst was 2 g L^{-1}. The photocatalyst was recycled after filtrating and heating treatment at 100 °C for 8 h for every cycle. The results are shown in Figure 10. The degradation efficiency of the catalyst in all the five runs is 1st run to 3rd runs 93, 93, 93%, 4th and 5th runs 98 and 98% degradation at 120 min.

**Mechanism**

A possible mechanism involved in the formation of TiO2/Bi2O4 nanocomposite is predicted from Figure 11. Considering the band positions, the conduction band (CB) and valence band (VB) of Bi2O4 were
found at +0.649 and +2.619 eV, respectively and those of TiO$_2$ were observed at –0.335 and +2.895 eV, respectively. The appropriate band positions of TiO$_2$ and Bi$_2$O$_4$ promote the formation of the heterojunction structure and enhance the photocatalytic activity. Under light irradiation, the photoexcited electrons in the CB of TiO$_2$ can jump to the CB of Bi$_2$O$_4$. The CB potential of Bi$_2$O$_4$ was found to be more electronegative than the reduction potential of O$_2$ /O$_2$·– (–0.34 eV Vs NHE), and therefore the electrons concentrated in the CB of Bi$_2$O$_4$ can generate O$_2$·– for dye degradation. Meanwhile the holes on the VB bands of TiO$_2$ and Bi$_2$O$_4$ oxidize H$_2$O to produce OH, and it is a highly oxidative species towards dye degradation. The band gap energy obtained by Kubelka-Munk (KM) function is comparatively lower than pure undoped TiO$_2$.

**Conclusion**

Nanocomposites of TiO$_2$/Bi$_2$O$_4$ synthesized by sol-gel method. The nanocomposite characterized by FT-IR, XRD, SEM-EDX and UV-Vis-DRS analysis. Photocatalytic decomposition of EY was analysed with different pHs and reusability. Analysis of the reusability of the catalyst revealed that the catalyst is stable and reusable. A suitable degradation mechanism was also proposed.

**References**


